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REACTION OF SOME D-GLUCOBIOSES WITH 2,2-DIMETHOXYPROPANE

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ABSTRACT

Laminarabiose, cellobiose, and gentiobiose were acetonated with 2,2-dimethoxypropane under various conditions. Two isopropylidene acetals in which the reducing D-glucose residue had the furanoid form were obtained from laminarabiose, and two, in which the reducing D-glucose residue formed the acyclic dimethyl acetal, from cellobiose. Gentiobiose gave both types of isopropylidene compound.

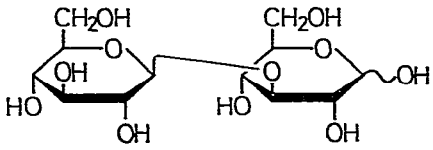
INTRODUCTION

Isopropylidene acetals of carbohydrates are important as intermediates for the synthesis of other sugar derivatives[1–3]. The acetonation of various monosaccharides[4–10] and disaccharides[11–17] with 2,2-dimethoxypropane, or ethyl isopropenyl ether, in *N*,*N*-dimethylformamide in the presence of *p*-toluenesulfonic acid has been studied, and has yielded many useful derivatives. It has been found that the reaction is kinetically controlled, with favored attack on the primary hydroxyl group by the reagent.

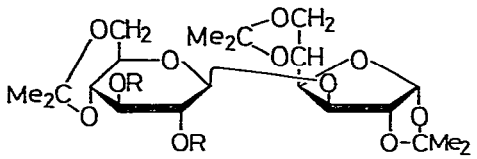
In a previous paper[18], we reported that acetonation of maltose with 2,2-dimethoxypropane in *N*,*N*-dimethylformamide and 1,4-dioxane[19] yielded some interesting derivatives, such as compounds having an isopropylidene group bridging two D-glucose residues, and acyclic dimethyl acetal compounds. In continuation of the study, we now describe the result of acetonation of laminarabiose, cellobiose, and gentiobiose with 2,2-dimethoxypropane under a variety of conditions.

RESULTS AND DISCUSSION

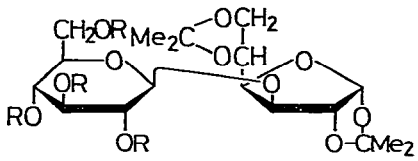
Treatment of laminarabiose (**1**) with an excess of 2,2-dimethoxypropane in dry *N*,*N*-dimethylformamide in the presence of a trace of *p*-toluenesulfonic acid (1 mg/mL of the solvent) at 80° (reaction *A*) gave **2** as the main product, and it was separated on a column of silica gel by chromatography. The n.m.r. spectrum of the acetate (**3**) of **2** showed the presence of two acetyl and three isopropylidene groups. The chemical shift of the signal for H-1 (d, δ 5.8) indicated the presence of a 1,2-*O*-isopropylidene-D-glucofuranose residue. The mass spectrum of **3** showed the parent-



1



2 R=H
3 R=Ac



4 R=H
5 R=Ac

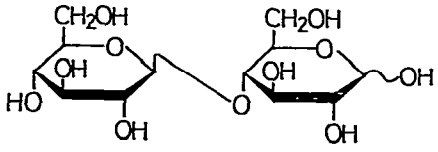
ion peak at *m/z* 531 ($M^+ - CH_3$), and peaks at *m/z* 287 and 101, which are strongly indicative of the presence of a di-*O*-acetyl-*O*-isopropylidene-D-glucofuranose residue and a 5,6-*O*-isopropylidene group, respectively. The most probable structure of **3** is 3-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose.

On the other hand, when this treatment was performed in the presence of an excess of *p*-toluenesulfonic acid (reaction *B*), compound **4** was obtained, together with **2**. The n.m.r. spectrum of the acetate (**5**) of **4** showed the presence of a 1,2-*O*-isopropylidene-D-glucofuranose residue. In addition to the ion peaks at *m/z* 575 ($M^+ - CH_3$) and 101, the ion peak at *m/z* 331, which was assigned to the tetra-*O*-acetyl-D-glucose ion, was detected in the mass spectrum, indicating that **5** is 1,2:5,6-di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucofuranose.

When 1,4-dioxane was used as the solvent in this reaction (reaction *C*), laminarabiose (**1**) gave **2**, in which the (reducing) D-glucose residue forms a furanoid ring, but no acyclic dimethyl acetal derivatives

Treatment of cellobiose (**6**) with an excess of 2,2-dimethoxypropane in dry *N*,*N*-dimethylformamide in the presence of *p*-toluenesulfonic acid at room temperature, and at 80°, yielded too many products to isolate and identify. However, when this treatment was performed at 80°, using 1,4-dioxane as the solvent instead of *N*,*N*-dimethylformamide, two major products, **7** and **9**, were obtained, although an attempted reaction at room temperature did not proceed.

The n.m.r. spectrum of the acetate (**8**) of **7** evidenced the presence of two acetyl, three isopropylidene, and two methoxyl groups, and its mass spectrum showed ion peaks at *m/z* 577 ($M^- - CH_3$), 287, 101, and at *m/z* 75, assigned to $C^+H(OMe)_2$ as indicative of an aldehyde dimethyl acetal. Thus, the most probable structure of **8** is 4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal.



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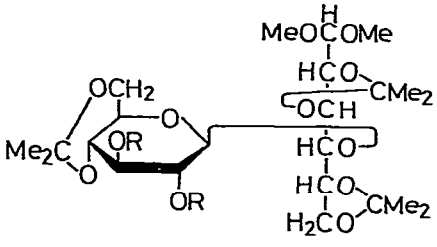

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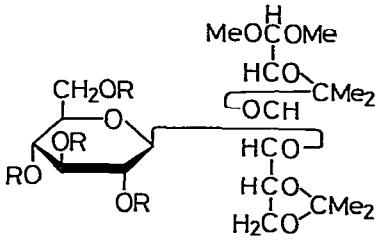
8 R = Ac



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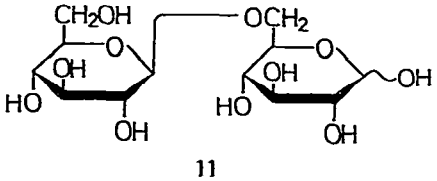
10 R = Ac



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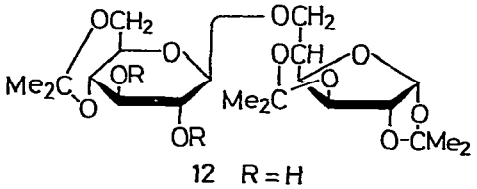
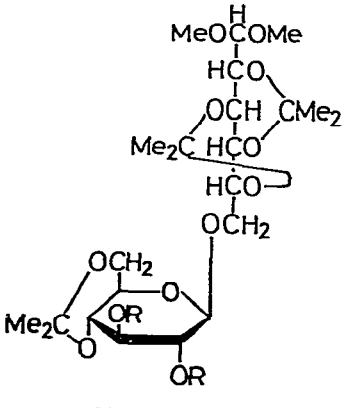
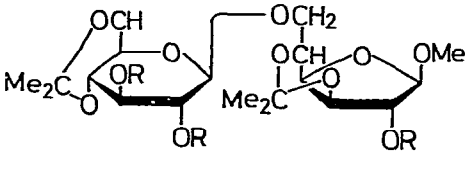


12 R = H
13 R = Ac



14 R = H
15 R = Ac



16 R = H
17 R = Ac

The n.m.r. spectrum of the acetate (**10**) of **9** indicated the presence of four acetyl, two isopropylidene, and two methoxyl groups, and its mass spectrum showed ion peaks at *m/z* 621, 331, 101, and 75. Therefore, the structure of **10** was determined to be 2,3:5,6-di-*O*-isopropylidene-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-*aldehydo*-D-glucose dimethyl acetal.

Acetonation of gentiobiose (**11**) with 2,2-dimethoxypropane in *N,N*-dimethylformamide gave a mixture affording many spots in t.l.c., and the products could not be separated to yield a single, pure compound. Treatment of **11** with an excess of 2,2-dimethoxypropane in dry 1,4-dioxane in the presence of *p*-toluenesulfonic acid at 80° gave **12**, **14**, and **16**. The major product was separated by column chromatography, and gave only one spot in t.l.c., but its n.m.r. spectrum showed that it was a mixture of two kinds of compound, namely, **12** and **14**. These could be separated by column chromatography of their acetyl derivatives. The mass spectrum indicated that the acetyl derivative (**13**) of **12** contained a 2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-D-glucopyranosyl group, and the n.m.r. spectrum showed the presence of three kinds of isopropylidene group, one of which could be assigned to a 1,2-*O*-isopropylidene group on a D-glucofuranose residue. Therefore, the structure of **13** was determined to be 6-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose.

The mass spectrum of the acetate (**15**) derived from another component (**14**) showed the presence of a 2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-D-glucopyranosyl group and a dimethyl acetal group. Moreover, **15** contained three kinds of isopropylidene group, as revealed by the n.m.r. spectrum. One of them could be readily assigned to the 4,6-*O*-isopropylidene group, but the position of the two other groups could not be determined to be 2,3:4,5, 2,4:3,5, or 2,5.3,4 on the hydroxyl groups of the D-glucose residue. One of the groups was probably assignable as a 3,5-*O*-isopropylidene group, by inference from the structures of **13** and **17**. Thus, the structure of **15** was tentatively assigned as 6-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-2,4:3,5-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal.

The n.m.r. spectrum of the acetate (**17**) of the minor product **16** (obtained by column chromatography) showed the presence of one methoxyl, three acetyl, and two isopropylidene groups. The coupling constant of the signal for H-1 (δ 4.83, 0 Hz) indicated the presence of a β-furanoside residue. Its mass spectrum showed ion peaks at *m/z* 547 ($M^+ - CH_3$) and 287. Therefore, **17** is methyl 2-*O*-acetyl-6-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-3,5-*O*-isopropylidene-β-D-glucofuranoside.

Acetonation of laminarabiose (**1**) in the presence of an excess of *p*-toluenesulfonic acid yielded **4** as well as **2** as the main products, whereas reaction in the presence of a trace of the acid afforded only **2**. Assuming that this acetonation is kinetically controlled, with favored attack on the primary hydroxyl group, compound **4** is not a precursor of **2**, but is a compound derived from **2** by hydrolysis of the 4,6-*O*-isopropylidene group during the reaction with an excess of the acid, indicating that the

4,6-*O*-isopropylidene is more labile than the 5,6-*O*-isopropylidene group. The acetonation of cellobiose involved a similar phenomenon.

It has been reported[19] that dimethyl acetal compounds are formed mainly in the acetonation of monosaccharides when 1,4-dioxane is used as the solvent. Interestingly, the corresponding dimethyl acetal was similarly obtained from cellobiose, but not from laminarabiose. This may be explained as follows: in laminarabiose (**1**), it is easy for the reducing D-glucose residue to form a furanose ring after attachment of the 5,6-*O*-isopropylidene group, as its 4-hydroxyl group is free. The formation of this furanose ring is then followed by isopropylidenation of the 1- and 2-hydroxyl groups, to yield compounds **2** and **4**. In the case of cellobiose (**6**), as the 4-hydroxyl group of the (reducing) D-glucose residue is already substituted by a D-glucosyl group, the reducing residue cannot form a furanose ring, and, consequently, the acyclic, dimethyl acetal compounds **7** and **9** are obtained.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined with a Union PM-201 polarimeter. Preparative chromatography was performed on Silica Gel (Wako Co.; 200 mesh) with the solvent systems specified. *N*,*N*-Dimethylformamide and 1,4-dioxane were distilled before use. Evaporations were conducted *in vacuo*. N.m.r. spectra were recorded at 90 MHz with a Hitachi R-22 spectrometer for solutions in chloroform-*d*; tetramethylsilane was used as the internal standard, and the sample temperature was 35°. Chemical shifts are given as δ values, and the couplings recorded are first-order spacings. Mass spectra were recorded with a Hitachi RMU-6M spectrometer operating at 70 eV.

Acetonation of laminarabiose (**1**). — *Reaction* A. To a stirred solution of laminarabiose (**1**; 200 mg, 0.58 mmol) in *N*,*N*-dimethylformamide (2 mL) were added *p*-toluenesulfonic acid (2 mg, 1 mg/mL of the solvent) and then 2,2-dimethoxypropane (0.6 mL, 8.3 mol/mol of **1**). The mixture was stirred for 5 h at 80°, cooled, and then treated with Amberlite IRA-410 (OH^-) resin to remove the acid. The resin was filtered off, and washed with methanol. The combined filtrate and washings were evaporated, and the syrupy residue was chromatographed on a column (2 cm diam.) of silicic acid (7 g) with chloroform and chloroform–methanol mixtures. A 70:1 chloroform–methanol eluate yielded syrupy **2** (170 mg, 63%).

3-O-(*2,3-Di*-O-*acetyl-4,6*-O-*isopropylidene-β*-D-*glucopyranosyl*)-*1,2*:*5,6-di*-O-*isopropylidene-α*-D-*glucofuranose* (**3**). — The syrupy **2** was acetylated with acetic anhydride–pyridine, and the product crystallized from ethanol; m.p. 175–176°, $[\alpha]_D^{20}$ −20° (*c* 0.18, chloroform); n.m.r.: δ 1.30, 1.33, 1.38, 1.40, and 1.48 (5 s, 3 Me_2C), 2.04 (2 AcO), 4.7 (t, $J_{1',2'} = J_{2',3'} = 8$ Hz, H-2'), 4.93 (d, $J_{1,2}$ 8 Hz, H-1'), 5.1 (t, $J_{2',3'} = J_{3',4'} = 9$ Hz, H-3'), and 5.8 (d, $J_{1,2}$ 4 Hz, H-1); *m/z* 531 (31, $M^+ - CH_3$), 445 (3), 413 (5), 355 (3), 287 (24), 273 (6), 229 (5), 227 (19), 169 (30), 127 (21), 109 (15), 101 (100), and 43 (75, MeC^+O).

Reaction B. To a stirred solution of laminarabiose (**1**; 200 mg) in *N,N*-dimethylformamide (2 mL) were added *p*-toluenesulfonic acid (30 mg, 15 mg/mL of the solvent) and then 2,2-dimethoxypropane (0.6 mL, 8.3 mol/mol of **1**). The mixture was stirred for 15 min at 80°, cooled, and then treated with Amberlite IRA-410 (OH^-) resin to remove the acid. The resin was filtered off, and washed with methanol. The filtrate and washings were combined and evaporated, and the syrupy residue was chromatographed on a column of silicic acid (7 g) with chloroform and chloroform–methanol mixtures. A syrup of **2** (80 mg, 30%) was recovered from a 70:1 chloroform–methanol eluate, and syrupy **4** (90 mg, 37%) from a 30:1 chloroform–methanol eluate.

*1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-α-*D*-glucofuranose* (**5**). — The syrupy **4** was acetylated with acetic anhydride–pyridine, and the product (**5**) crystallized from ethanol; m.p. 133–134°, $[\alpha]_D^{20}$ −57° (*c* 0.2, chloroform); n.m.r.: δ 1.30, 1.35, 1.45, and 1.50 (4 s, 2 Me_2C), 2.0–2.1 (4 s, AcO), 4.67 (d, $J_{1',2'}$ 7 Hz, H-1'), 4.8–5.2 (3 H), and 5.8 (d, $J_{1,2}$ 4 Hz, H-1); *m/z* 575 (41, $M^+ - CH_3$), 517 (3), 489 (7), 331 (56), 273 (5), 271 (14), 229 (5), 201 (3), 169 (90), 127 (26), 109 (49), 101 (87), and 43 (100, MeC^+O).

Reaction C. Laminarabiose (**1**; 200 mg) was acetonated in 1,4-dioxane (3 mL) with 2,2-dimethoxypropane (1 mL, 14 mol/mol of **1**) and *p*-toluenesulfonic acid (30 mg, 10 mg/mL of the solvent) for 3 h at 80°. The mixture was cooled, treated with Amberlite IRA-410 (OH^-) resin, the suspension filtered, and the filtrate evaporated to a syrup which was chromatographed on a column (2 cm diam.) of silicic acid (7 g) with chloroform and chloroform–methanol mixtures. A 70:1 chloroform–methanol eluate yielded a syrup of **2** (130 mg, 48%), which was characterized as already described.

Acetonation of cellobiose (**6**). — 2,2-Dimethoxypropane (0.9 mL, 8.3 mol/mol of **6**) and *p*-toluenesulfonic acid (40 mg, 13 mg/mL of the solvent) were added to a suspension of cellobiose (**6**), and the mixture was kept for 24 h at 80°, with stirring. The mixture was cooled, the acid neutralized with Amberlite IRA-410 (OH^-) resin, the suspension filtered, and the filtrate evaporated to a syrup which was subjected to chromatography on a column (2 cm diam.) of silicic acid (10 g). Syrupy **7** (100 mg, 23%) was isolated from a 70:1 chloroform–methanol eluate, and **9** (215 mg, 53%) from a 20:1 $CHCl_3$–MeOH eluate.

*4-O-(2,3-Di-*O*-acetyl-4,6-*O*-isopropylidene-β-*D*-glucopyranosyl)-2,3:5,6-di-*O*-isopropylidene*-aldehydo-*D*-*glucose dimethyl acetal* (**8**). — The syrupy **7** was acetylated with acetic anhydride–pyridine, to give **8**, $[\alpha]_D^{20}$ −34° (*c* 0.89, chloroform); n.m.r.: δ 1.3–1.5 (3 Me_2C), 2.02 and 2.08 (2 AcO), 3.4 (2 MeO), and 4.85–5.2 (3 H); *m/z* 577 (7, $M^+ - CH_3$), 517 (2), 303 (5), 287 (9), 227 (9), 169 (20), 141 (13), 127 (9), 115 (24), 101 (55), 85 (60), 83 (63), 75 (58), and 43 (100, MeC^+O).

*2,3:5,6-Di-*O*-isopropylidene-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-*aldehydo-*D*-*glucose dimethyl acetal* (**10**). — The syrupy **9** was acetylated with acetic anhydride–pyridine, to give **10**, $[\alpha]_D^{20}$ −12° (*c* 0.51, chloroform); n.m.r.: δ 1.3–1.5 (2 Me_2C), 2.00, 2.02, 2.08, and 2.10 (4 s, AcO), 3.38 and 3.40 (2 s, MeO), and 4.9–5.2

(4 H); *m/z* 621 (10, $M^+ - CH_3$), 331 (19), 169 (74), 127 (20), 115 (32), 109 (44), 101 (43), 85 (21), 75 (55), 73 (45), and 43 (100, MeC^+O).

Acetonation of gentiobiose (**11**). — Gentiobiose (**11**; 400 mg, 1.17 mmol) was acetonated in 1,4-dioxane (8 mL) with 2,2-dimethoxypropane (2 mL, 13.8 mol/mol of **11**) and *p*-toluenesulfonic acid (20 mg, 2.5 mg/mL of the solvent) for 4 h at 80°. The mixture was cooled, and treated with Amberlite IRA-410 (OH^-) resin to remove the acid. The resin was filtered off, and washed with methanol, and the filtrate and washings were combined, and evaporated. The syrupy residue was chromatographed on a column (2 cm diam.) of silicic acid (12 g) with chloroform and chloroform–methanol mixtures. A 70:1 chloroform–methanol eluate yielded a mixture (220 mg) of **12** and **14** that showed a single spot in t.l.c Syrupy compound **16** (47 mg, 9.2%) was isolated from a 25:1 $CHCl_3$–MeOH eluate.

6-O-(2,3-Di-O-acetyl-4,6-O-isopropylidene-β-D-glucopyranosyl)-1,2·3,5-di-O-isopropylidene-α-D-glucofuranose (**13**) *and 6-O-(2,3-di-O-acetyl-4,6-O-isopropylidene-β-D-glucopyranosyl)-2,4:3,5-di-O-isopropylidene*-aldehydo-D-*glucose dimethyl acetal* (**15**) — The mixture of **12** and **14** was acetylated with acetic anhydride–pyridine, to give **13** plus **15**. The acetates were placed on a column (1.5 cm diam.) of silicic acid (7 g), and eluted with chloroform–methanol mixtures.

The first part of a 400:1 chloroform–methanol eluate afforded **13**, which crystallized from ethanol; m.p. 118–119°, $[\alpha]_D^{20}$ −19° (*c* 1.56, chloroform); n.m.r.: δ 1.33–1.48 (3 Me_2C), 2.01 (2 AcO), 4.52 (d, $J_{1,2}$ 4 Hz, H-2), 4.6 (d, $J_{1',2'}$ 8 Hz, H-1'), 4.93 (dd, $J_{1',2'}$ 8, $J_{2',3'}$ 9 Hz, H-2'), 5.11 (t, $J_{2',3'} \approx J_{3',4} = 9$ Hz, H-3'), and 5.95 (d, $J_{1,2}$ 4 Hz, H-1); *m/z* 531 (18, $M^+ - CH_3$), 287 (14), 273 (16), 229 (14), 227 (14), 169 (38), 129 (30), 127 (42), 113 (100), 109 (30), 101 (80), 85 (44), 59 (84), and 43 (90, MeC^+O).

The latter part of the eluate afforded **15** as a syrup; $[\alpha]_D^{20}$ −36° (*c* 0.58, chloroform); n.m.r.: δ 1.33–1.48 (3 Me_2C), 2.02 (2 AcO), 3.42 and 3.43 (2 s, MeO), 4.63 (d, $J_{1',2'}$ 8 Hz, H-1'), 4.9 (dd, $J_{1',2}$ 8, $J_{2',3'}$ 9 Hz, H-2'), 5.13 (t, $J_{2',3} \approx J_{3',4} = 9$ Hz, H-3'); *m/z* 577 (25, $M^+ - CH_3$), 517 (6), 287 (34), 227 (30), 169 (66), 141 (34), 127 (45), 115 (100), 113 (37), 109 (37), 101 (90), 99 (37), 85 (69), 75 (80), 73 (70), 59 (84), and 43 (100, MeC^+O).

Methyl 2-O-acetyl-6-O-(2,3-di-O-acetyl-4,6-O-isopropylidene-β-D-glucopyranosyl)-3,5-O-isopropylidene-β-D-glucofuranoside (**17**). — The syrupy **16** was acetylated with acetic anhydride–pyridine, and the acetate (**17**) crystallized from ethanol; m.p. 166–167°, $[\alpha]_D^{20}$ −5° (*c* 0.36, chloroform); n.m.r.: δ 1.33, 1.35, 1.37, and 1.45 (4 s, Me_2C), 2.02 and 2.06 (2 s, 3 AcO), 3.33 (s, MeO), 4.61 (d, $J_{1',2'}$ 8 Hz, H-1'), 4.83 (s, H-1), 4.92 (t, $J_{1',2'} = J_{2',3'} = 8$ Hz, H-2'), 5.07 (s, H-2), and 5.1 (t, $J_{2',3'} = J_{3',4'} = 8$ Hz, H-3'); *m/z* 547 (6, $M^+ - CH_3$), 531 (3), 287 (9), 227 (10), 187 (16), 169 (38), 159 (46), 141 (26), 127 (42), 115 (28), 109 (33), 103 (27), 99 (45), and 43 (100, MeC^+O).

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